
Sum and Density of States of Polyatomic Systems with Hindered Rotors

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ABSTRACT

The density or sum of states for a collection of independent oscillators, free rotors, and one-dimensional hindered rotors is obtained with good accuracy by numerical inversion of the corresponding total partition function by the method of steepest descents. The hindered-rotor partition functions are used in both classical and quantum forms, the latter in the approximation proposed by Truhlar [*J. Comput. Chem.*, **12**, 266 (1991)]. The numerical inversion compares well with analytical results obtained in a simple artificial case and also with an exact count of states in a large ethane-like system. Inversion of the hindered-rotor classical partition function is shown to lead to a somewhat different energy dependence of the sum or density of states, relative to the quantum counterpart, which is considered to be a more realistic representation. The routines presented are simple and fast enough to be of use in microcanonical rate calculations.
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Introduction

A number of molecules, for example, CH_3OH or C_2H_6 (and most aliphatic and olefinic hydrocarbons), possess a degree of freedom of internal rotation of (at least) one part of the molecule against the other; specifically of the CH_3 group against OH or against another CH_3 group in the two examples cited. This one-dimensional rotation is generally opposed by a potential barrier which causes the rotation to be hindered at energies below and to some extent above the barrier.

As a consequence, the barrier affects, among other things, the calculated thermodynamic properties of the molecule. An analysis of the problem by Pitzer¹ many years ago was done with a view to obtaining appropriate corrections to free-rotor thermodynamic functions, assuming that the molecule can be regarded as a rigid frame with attached symmetrical tops. Except in the purely classical case, the problem is not amenable to a closed-form solution, so that Pitzer presented his results in the form of tables for a selection of barrier heights and moments of inertia.

Another domain where the hindered-rotor problem is of some importance is in rate calculations,

as in microcanonical unimolecular rate theory (e.g., Rice–Ramsperger–Kassel–Marcus calculations and variational variants thereof), where one requires the sum or density of states for all so-called active degrees of freedom of the entire molecule, usually vibrations plus internal rotors (if there are several), plus any external rotor that may become active, as, for example, the *K*-rotor in a symmetric top.²

Strictly speaking, there is no hindered-rotor “problem” in the sense that if its energy levels are known and all active degrees of freedom are assumed to be separable, the appropriate sum of states can be obtained fairly easily by the Beyer–Swinehart exact count algorithm,^{3,4} at least if the energy is not too high.

The difficulty is that it takes a rather arduous calculation to obtain the hindered-rotor energy levels, which complicates the already involved rate calculation. Thus for practical reasons there is a need for a rapid calculation of the combined sum or density of states of all active degrees of freedom by a simple and reasonably accurate approximation. This paper is specifically addressed to this aspect of the hindered-rotor question.

Theory

The potential hindering an internal rotor is generally assumed to be of the form

$$V(\phi) = \frac{1}{2} V_0 (1 - \cos \sigma \phi) \quad (1)$$

where V_0 is the barrier height and σ is the number of equivalent potential minima. This is a convenient mathematical form of $V(\phi)$ believed to be semiquantitatively correct in most cases; it represents the lowest-order term in a Fourier expansion of the potential.

The solution for the energy levels with this potential is not easy because of complicated boundary conditions, but if $\cos \sigma \phi$ is expanded for small ϕ and all terms beyond the quadratic are dropped, the potential simplifies to $V(\phi) \approx V_0 \sigma^2 \phi^2 / 4$, for which the solution⁵ amounts to a harmonic oscillator with frequency $\omega = \sigma(AV_0)^{1/2}$, where $A = \hbar / 2I_r$ ($\hbar = h / 2\pi$; h = Planck's constant) is the rotational constant of the one-dimensional rotor and I_r is its moment of inertia. If the internal rotation involves the relative motion of two tops (with moments of inertia, say, I_1 and I_2) about their common bond, as in the examples above, then $I_r = I_1 I_2 / (I_1 + I_2)$, which represents the *reduced* moment of inertia. For sev-

eral attached tops the relation for I_r is likely to be more complicated.¹

The above result for small ϕ is valid for oscillator energies near the bottom of the potential. Assuming this oscillator to behave classically, the sum of states is then $G(E) = E/h\nu = E/\sigma(AV_0)^{1/2}$. At energies sufficiently above the barrier the rotor approaches a free rotor with sum of states given by $G(E) = (2/\sigma)(E/A)^{1/2}$. The anticipation is therefore that with increasing energy the nature of the hindered rotor will change from essentially a harmonic oscillator to a free rotor, with a changeover in the vicinity of V_0 .

The most general and convenient method for calculating the sum $[G(E)]$ or density $[N(E)]$ of states of a system of many degrees of freedom at energy E is to take the inverse Laplace transform $\mathcal{L}^{-1}\{\dots\}$ of the corresponding partition function Q , which is the approach that will be used here throughout. With $\beta = 1/kT$ the transform parameter (k = Boltzmann's constant; T = temperature), it can be shown that⁶

$$\left. \begin{array}{l} N(E)_{u=0} \\ G(E)_{u=1} \end{array} \right\} = \mathcal{L}^{-1} \left\{ \frac{Q(s)}{\beta^u} \right\} \quad (2)$$

where the parameter u selects the sum or density, given that the sum of states $G(E)$ is the integral of the density $N(E)$. If the system is simple enough, analytic inversion is possible; if not, inversion can be done numerically.

The hindered-rotor partition function and its inversion take different forms in classical and quantum terms. The classical case will be discussed first.

CLASSICAL HINDERED ROTOR

The classical partition function for a one-dimensional rotor with moment of inertia I_r and Hamiltonian H that includes the hindering potential $V(\phi)$ is

$$Q_{1h} = \frac{1}{h} \int e^{-H/kT} dp_\phi d\phi$$

$$H = \frac{p_\phi^2}{2I_r} + V(\phi) \quad (3)$$

Integration with respect to the momentum p_ϕ can be done immediately, so that using eq. (1) and

$A = \hbar/2I_r$, $b = V_0/2kT$, $x = \sigma\phi$, the result is

$$Q_{1h} = \left(\frac{kT}{\pi A}\right)^{1/2} \frac{e^{-b}}{\sigma} \int_0^\pi e^{b \cos x} dx \quad (4)$$

where the integral represents π times $I_0(b)$, the modified Bessel function of order zero.^{7a} The final result is thus

$$Q_{1h} = Q_{1f} e^{-b} I_0(b) \quad (5)$$

where $Q_{1f} = q_{1f}(kT)^{1/2}$, with $q_{1f} = (1/\sigma)(\pi/A)^{1/2}$, is the partition function for the corresponding one-dimensional free rotor of symmetry number σ .

Since eq. (5) represents the classical case, i.e., the limiting case of high temperature or high moment of inertia, thermodynamic functions calculated on this basis are labeled by Pitzer¹ in his tables as representing the case $1/Q_{1f} = 0$. Knyazev et al.⁸ have obtained the density of states corresponding to the partition function of eq. (5) from the analytic inverse Laplace transform of $e^{-b} I_0(b)$ in the form

$$N(E) = \begin{cases} \frac{2q_{1f}}{\pi^{3/2} V_0^{1/2}} \mathcal{K}\left(\frac{E}{V_0}\right), & E < V_0 \\ \frac{2q_{1f}}{\pi^{3/2} E^{1/2}} \mathcal{K}\left(\frac{V_0}{E}\right), & E > V_0 \end{cases} \quad (6)$$

where $\mathcal{K}(m)$ is the complete elliptic integral of the first kind^{7b} [eq. (6) uses for $\mathcal{K}(m)$ the definition of ref. 7]. An example of the energy dependence of $N(E)$ calculated from eq. (6) is shown in Figure 1.

When $E \rightarrow V_0$, $\mathcal{K}(1) \rightarrow \infty$, so that the above density $N(E)$ goes off to infinity when energy reaches the vicinity of the barrier height. Although the corresponding sum of states $G(E)$ remains

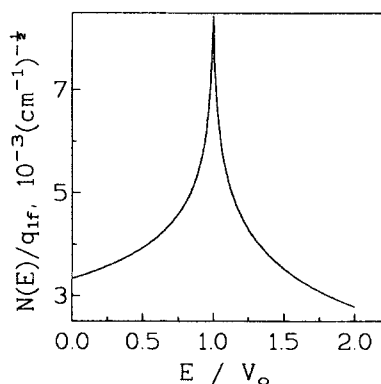


FIGURE 1. Energy dependence of $N(E)/q_{1f}$ calculated from eq. (6), assuming $V_0 = 1000 \text{ cm}^{-1}$.

finite, showing only a slight kink as $E \rightarrow V_0$, the sort of behavior shown in Figure 1 is not very convenient and is impossible to reproduce by a numerical approach.

However, in the context of rate calculations, the density (or the sum of states) of a hindered rotor is not required as such, but always as part of a combined density of a larger system, which has the effect of smoothing out any discontinuity at $E = V_0$. Thus Robertson and Wardlaw⁹ obtained by analytic inversion the combined density of states of a system of three free rotors plus one hindered rotor (a model for propylene) in the form

$$N(E) = \begin{cases} \frac{q_4 V_0}{2\pi} \{(1 - \alpha^2)^{1/2} - \alpha \arccos \alpha\}, & E < V_0 \\ q_4 \left(E - \frac{1}{2} V_0\right), & E > V_0 \end{cases} \quad (7)$$

where $\alpha = 1 - 2E/V_0$ and $q_4 = Q_4/(kT)^2$, Q_4 being the complete classical partition function for four free rotors; the parentheses above correct for the hindering of the fourth rotor. This density has no discontinuity at $E = V_0$ since $N(E = V_0) = \frac{1}{2} q_4 V_0$. The interest of this demonstration is to show that when the hindered rotor is considered as part of a larger system, the combined density of states exhibits no discontinuity, which augurs well for a numerical approach.

However, even as simple a case as three free rotors plus two independent hindered rotors (a model for isopropyl radical) is no longer amenable to analytical solution.⁹

Consider now a system composed of v quantum oscillators, r classical free rotors, and n classical hindered rotors. We shall assume for simplicity that all hindered rotors have the same properties (as, for example, the methyl groups in the isopropyl radical), but this is not essential. If these degrees of freedom are assumed to be separable, in particular that the hindered rotors do not interact, the total partition function is the product $Q_{\text{tot}} = Q_v Q_r (Q_{1h})^n$, where Q_{1h} is given by eq. (5) and $Q_r = q_r(kT)^{r/2}$, q_r being the part of the partition function for r free rotors in which the kT part has been dropped. The convention here is that a j -dimensional rotor counts for j rotations.

Except in trivial cases, inversion of such a general partition function cannot be done analytically, so that numerical inversion is necessary. Using eqs. (2) and (5), the inversion integral for the sum

and density of states, with $\beta = 1/kT$, is⁶

$$\left. \begin{aligned} N(E)_{u=0} \\ G(E)_{u=1} \end{aligned} \right\} = \frac{q_r(q_{1f})^n}{2\pi i} \times \int_{c-i\infty}^{c+i\infty} \frac{Q_v(\beta)(I_0(a\beta))^n e^{\beta(E-na)} d\beta}{\beta^{u+(r+n)/2}} \quad (8)$$

where $a = \frac{1}{2}V_0$. The inversion integral is conveniently evaluated by the method of steepest descents. To this end, define a function $\phi(\beta)$ which is the logarithm of the integrand

$$\phi(\beta) = \ln Q_v(\beta) + n \ln I_0(a\beta) + \beta(E - na) - \frac{1}{2}(r + n + 2u) \ln \beta \quad (9)$$

The approximation to the sum or density, to first order, is then

$$\left. \begin{aligned} N(E)_{u=0} \\ G(E)_{u=1} \end{aligned} \right\} = \frac{q_r(q_{1f})^n e^{\phi(\beta^*)}}{[2\pi\phi''(\beta^*)]^{1/2}} \quad (10)$$

where β^* is the solution of $\partial\phi/\partial\beta = 0$. This is a transcendental equation easily solvable by Newton-Raphson iteration, whereby β_{i+1} , the $(i+1)$ st approximation to β^* , is given in terms of the preceding β_i , i.e., by $\beta_{i+1} = \beta_i - (\partial\phi/\partial\beta)_i / (\partial^2\phi/\partial\beta^2)_i$. $\phi''(\beta^*)$ is the second derivative $\partial^2\phi/\partial\beta^2$ evaluated at $\beta = \beta^*$, which does not have to be computed again since it is available from the last iteration. The derivatives of $I_0(a\beta)$ can be obtained analytically in terms of modified Bessel functions of higher order.^{7a} Thus

$$\frac{\partial\phi(\beta)}{\partial\beta} = \frac{\partial \ln Q_v(\beta)}{\partial\beta} + (E - na) + n \frac{aI_1(a\beta)}{I_0(a\beta)} - \frac{r + n + 2u}{2\beta} \quad (11)$$

$$\begin{aligned} \frac{\partial^2\phi(\beta)}{\partial\beta^2} = & \frac{\partial^2 \ln Q_v(\beta)}{\partial\beta^2} + \frac{n}{2} a^2 \left\{ 1 + \frac{I_2(a\beta)}{I_0(a\beta)} \right\} \\ & + \frac{r + n + 2u}{2\beta^2} - n \left\{ a \frac{I_1(a\beta)}{I_0(a\beta)} \right\}^2 \end{aligned} \quad (12)$$

where $I_m(x)$ is the modified Bessel function of order m . The vibrational partition function $Q_v(\beta)$ and its logarithmic derivatives are readily obtained analytically for separable oscillators—harmonic or anharmonic—as shown in the Appendix.

QUANTUM HINDERED ROTOR

The partition function in this case can be obtained only by summation over the actual energy levels. However, since the Gibbs free energy F is related to the partition function Q by $F = -kT \ln Q$, the partition function is available in Pitzer's tables¹ disguised as $(F - F_f)/T$, the increase of free energy of the hindered rotor (F) relative to the free energy of the free rotor (F_f), divided by temperature. The tabulation is in terms of the dimensionless parameters V_0/kT and $1/Q_{1f}$. Truhlar¹⁰ has proposed a simple interpolation formula to recover the quantum partition function from these tables with fairly good accuracy. With energy zero at ground state, his hindered-rotor partition function in terms of $\beta = 1/kT$ is

$$\begin{aligned} Q_{1h}(\beta) &= \frac{\tanh(\pi V_0 \beta)^{1/2}}{1 - e^{-\omega\beta}} \\ &= Q_{1v}(\beta) \tanh(\pi V_0 \beta)^{1/2} \end{aligned} \quad (13)$$

where $\omega = \sigma(AV_0)^{1/2}$ is the equivalent oscillator frequency mentioned above and thus $(1 - e^{-\omega\beta})^{-1} = Q_{1v}(\beta)$ is the corresponding partition function with energy zero at ground state. For small x , $\tanh x \rightarrow x$, so that for small β , i.e., at high temperature, $Q_{1h}(\beta) \rightarrow (\pi V_0 \beta)^{1/2}/\omega\beta = Q_{1f}$, which is the partition function of the corresponding classical free rotor, whereas $\tanh(\pi V_0 \beta)^{1/2} \rightarrow 1$ for large V_0 , so that $Q_{1h}(\beta) \rightarrow Q_{1v}(\beta)$. While these are the expected limiting values, compared with Pitzer's partition function, the approximation represented by eq. (13) gives, overall, low results for intermediate values of $V_0 \beta$: generally 10% or more too low for $V_0 \beta \leq 5$, about 5% too low for $5 \leq V_0 \beta \leq 10$, but only about 1% or less too low for $V_0 \beta \geq 10$.

Thus eq. (13) performs best at low and intermediate temperatures, so that Laplace transform inversion is likely to yield more accurate results at low, rather than high, energies. This is rather fortunate since hindering barriers are generally low, on the order of 1000 cm^{-1} or less, and it is precisely at below-barrier energies that the largest deviations from free-rotor behavior occur (results shown in Figure 4 confirm this expectation).

The total partition function for a large molecule with v quantum oscillators, r classical free rotors, and n hindered rotors can now be constructed as before by incorporating eq. (13) as n factors, so that the analogue of $\phi(\beta)$ of eq. (9) becomes, with all vibrational partition functions combined into

$$Q_v^{\ddagger}(\beta) = Q_v(\beta)(Q_{1v}(\beta))^n, \text{ with } b = (\pi V_0)^{1/2},$$

$$\phi(\beta) = \ln Q_v^{\ddagger}(\beta) + n \ln \tanh(b\beta^{1/2}) + \beta E - \frac{1}{2}(r+n+2u)\ln \beta \quad (14)$$

The solution then proceeds as before, with β^* given as the solution of $\partial\phi/\partial\beta = 0$. The derivatives of $\phi(\beta)$ in eq. (14) are

$$\frac{\partial\phi(\beta)}{\partial\beta} = \frac{\partial \ln Q_v^{\ddagger}(\beta)}{\partial\beta} + E + \frac{nb^2}{\beta^{1/2} \sinh(2b\beta^{1/2})} - \frac{r+n+2u}{2\beta} \quad (15)$$

$$\begin{aligned} \frac{\partial^2\phi(\beta)}{\partial\beta^2} &= \frac{\partial^2 \ln Q_v^{\ddagger}(\beta)}{\partial\beta^2} + \frac{r+n+2u}{2\beta^2} - \frac{nb^2}{\beta \sinh(2b\beta^{1/2})} \\ &\quad \times \left\{ \frac{1}{2b\beta^{1/2}} + \frac{1}{\tanh(2b\beta^{1/2})} \right\} \quad (16) \end{aligned}$$

The final result, to first order, is

$$\left. \frac{N(E)_{u=0}}{G(E)_{u=1}} \right\} = \frac{q_r e^{\phi(\beta^*)}}{[2\pi\phi''(\beta^*)]^{1/2}} \quad (17)$$

where, as before, g_r is the kT -independent part of the partition function for the r free rotors.

Results

As a first test, we shall compare results, obtained by the steepest-descent routine in both the classical and quantum versions [using $u = 0$ and $Q_v(\beta) = 1$], with the classical analytical results [eq. (7)] for the density of three rigid free rotors plus one hindered rotor. In order to make the comparison independent of the properties of the free rotors, the quantity calculated in Figure 2 as a function of energy is $N(E)/q_r$, where q_r is the kT -independent part of the three free-rotor partition functions. It is immediately obvious that the classical and quantum densities show a different energy dependence: the classical case shows an undercount below V_0 and an overcount above V_0 . In the classical case, the steepest-descent routine of eqs. (10)–(12) (barely discernable dotted line) is seen to be in excellent agreement with the analytic result, so that it can be safely presumed that the steepest-descent quantum result [eqs. (15)–(17)]

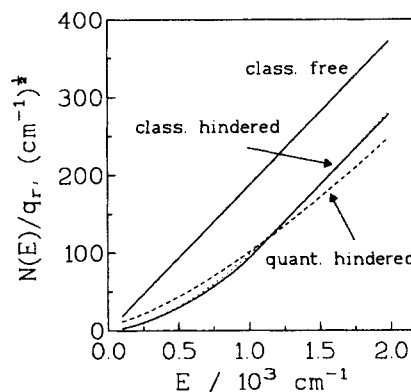


FIGURE 2. Energy dependence of $N(E)/q_3$ of a system consisting of three free rotors with partition function $Q_3 = q_3(kT)^{3/2}$ plus one one-dimensional hindered rotor subject to hindering potential $V_0 = 1000 \text{ cm}^{-1}$ with $\sigma = 3$ and $A = 10 \text{ cm}^{-1}$. These are parameters which apply roughly to the hindered rotor in ethane. Solid line: Analytic classical $N(E)$ of eq. (6) multiplied by $q_{1f} = (1/\sigma)(\pi/A)^{1/2}$. Dotted line (coincident with solid line over most of the range): Classical $N(E)$ by the method of steepest descents [eqs. (10)–(12)], multiplied by q_{1f} . Dashed line: Quantum $N(E)$ by the method of steepest descents [eqs. (15)–(17)]. The complete classical partition function for the four rotors is $Q_4 = q_4(kT)^2$, where $q_4 = q_3 q_{1f}$.

will be likewise a very good approximation.

To appreciate the difference if all four rotors were assumed free, Figure 2 shows also the corresponding classical free-rotor density given by $N(E)/q_r = E q_{1f}$. The discrepancy is substantial and disappears only at energies considerably above 1000 cm^{-1} , the assumed barrier height.

As a second test, take a system similar to above but with two hindered rotors for which analytical results are not possible. It is a simple matter to obtain the required result for the density $N(E)$ (Fig. 3) from the steepest-descent routines (using $u = 0$) in both the classical and quantum forms. Once again the classical version shows an undercount below the barrier (1000 cm^{-1}) and an overcount above.

For a third and more conclusive test, consider a larger ethane-like model system, composed of all oscillators in ethane, plus one internal hindered rotor. The Beyer–Swinehart algorithm³ is used to obtain the exact sum of states $G(E)$, which is then compared with the results of the above steepest-descent routines, using $u = 1$.

The parameters of the hindered-rotor model are $V_0 = 1000 \text{ cm}^{-1}$, $A = 11.1 \text{ cm}^{-1}$, and $\sigma = 3$, close enough to the actual hindered rotor in ethane,

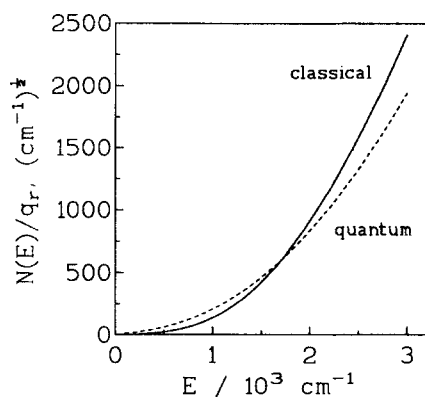


FIGURE 3. Energy dependence of $N(E)/q_3$ of a system consisting of three free rotors with partition $Q_3 = q_3(kT)^{3/2}$, as in Figure 2, plus two independent one-dimensional hindered rotors, each subject to hindering potential $V_0 = 1000 \text{ cm}^{-1}$ with $\sigma = 3$ and $A = 10 \text{ cm}^{-1}$. Solid line: Classical $N(E)$ by the method of steepest descents [eqs. (10)–(12)], multiplied by q_{1f} . Dashed line: Quantum $N(E)$ by the method of steepest descents [eqs. (15)–(17)].

selected to facilitate the calculation of energy levels from a tabulation by Wilson¹¹ of the eigenvalues of Mathieu's equation (see Table I). For the potential of eq. (1), the hindered-rotor energy levels relative to potential minimum are¹² $E = \frac{1}{2}V_0 + \frac{1}{4}A\sigma^2 \times \text{eigenvalue}$, so that in the present case $E = 500 + 25 \times \text{eigenvalue}$.

The exact count for this system is the solid staircase line shown in Figure 4 (these results reproduce those of Stein and Rabinovitch⁴). The dashed line is the smooth-function approximation obtained by inversion of the quantum partition function [eqs. (15)–(17)], and the dotted line is the result of the inversion of the classical partition function [eqs. (10)–(12)].

Similar to Figures 2 and 3, the inversion with the classical hindered-rotor partition function produces an undercount, while inversion using the

TABLE I.
Data for Figure 4.

Vibrational frequencies (cm^{-1}) of ethane oscillators,¹³ assumed to be harmonic and separable (degeneracies in parentheses): 821 (2), 995, 1206 (2), 1379, 1388, 1469 (2), 1472 (2), 2896, 2954, 2969 (2), 2985 (2). Energy levels (cm^{-1}), relative to ground state (at 152 cm^{-1}), of hindered internal rotor: 289, 541, 783, 876, 1284, 1286, followed by doubly degenerate free rotor energy levels given by $(500 - 152) + 25 \times (2n)^2$ for $n = 4, 5, \dots$. These levels reproduce Pitzer and Gwinn's¹ partition function within less than 1%.

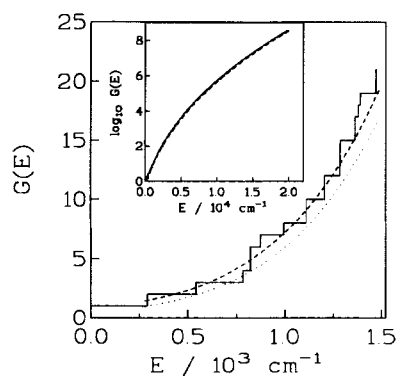


FIGURE 4. Energy dependence of the sum of states $G(E)$ for separable oscillators plus one hindered internal rotor in an ethane-like molecule. Staircase line: Exact count by the Beyer–Swinehart algorithm; dashed line: steepest-descent quantum approximation, eqs. (15)–(17); dotted line: steepest-descent classical approximation, eqs. (10)–(12). Inset: Semilog plot of data at high energies.

quantum hindered-rotor partition function yields a very good approximation below and somewhat above 1000 cm^{-1} , the hindering barrier height. Here the classical and quantum hindered-rotor results do not show a noticeably different energy dependence as in Figures 2 and 3. The reason is that the hindered rotor in ethane is only one among 18 degrees of freedom, so that the effect is considerably diluted.

The inset in Figure 3 shows a semilogarithmic plot of the results at high energies. Here both approximations produce a small undercount (which does not show much on the plot) due to the high-temperature behavior of the hindered-rotor partition functions. This is without practical consequences since at high energies the internal rotor is free, for which the steepest-descent approximation in its free-rotor version is virtually exact.

Conclusion

It is demonstrated that the density or sum of states for a collection of separable oscillators, classical free rotors, and hindered rotors (classical or quantum) can be obtained fairly easily and with good accuracy by numerical inversion of the corresponding total partition function by the method of steepest descents. Since the routines calculate directly the sum or density of states for large com-

posite systems, they make redundant the convolution of the densities for one kind of degree of freedom with another that would be otherwise required if the densities were calculated piecemeal for each kind separately. The numerical inversion compares well with analytical results obtained in a simple artificial case, and also with a direct exact count of states in a large ethane-like system.

The assumption used for simplicity in the example with two hindered rotors (Fig. 3) that both rotors have the same properties can be easily lifted. The modification to be made consists simply of replacing $(Q_{1h})^n$, the single hindered-rotor partition function to power n , by a product of n distinct partition functions, and similarly of replacing in eqs. (9), (11)–(12), and (14)–(16) the terms that have n (= number of hindered rotors) as a factor by a summation over n terms, each representing the distinct hindered rotor.

The quantum version [eqs. (15)–(17)], being more realistic, is the preferred one, which happens to be also the easiest to program, since it involves only hyperbolic functions which are found as primitives in most programming languages. The classical version [eqs. (10)–(12)], besides yielding a somewhat different energy dependence for the sum or density of states, is more computationally intensive since it requires the computation of the modified Bessel functions.

The limitations of the routines due to the approximations involved in the hindered-rotor treatment come from several sources: to begin with, eq. (1) is already an approximation; next several approximations are made by Pitzer¹ in the calculation of thermodynamic functions; finally there is the approximation represented by the interpolated partition function of eq. (13). For this reason it is probably not worthwhile to take the steepest-descent routines to second order, easily available at the price of a little more algebra. The assumption of all degrees of freedom being separable, in particular of individual hindered rotors not interacting, is imposed by the necessity of making the problem tractable. It is worth noting that even in a simple molecule like CH_3OH the hindered-rotor energy levels depend on overall rotation quantum number owing to the asymmetry of the two rotating parts.¹² Such a case cannot be treated by the present approach.

Subject to these limitations, the inversion routine is quite general and can accommodate any number of oscillators (not necessarily harmonic) and any number of free and hindered rotors, with only five iterations per energy on the average in

most cases, which makes it very fast indeed. It is thus well suited for microcanonical rate calculations. It will produce indifferently the sum or density of states by merely selecting 1 or 0, respectively, for the parameter u .

It should be mentioned that the present approach is not quite as simple in the case of a *two-dimensional* hindered rotor, such as appears, for instance, in the treatment of so-called transitional modes in the process $\text{CH}_4 \rightarrow \text{H} + \text{CH}_3$, inasmuch as the partition function for this rotor cannot be expressed in closed form.¹⁴ However, the corresponding sum and density of states is available analytically,¹⁵ so that in a large system comprising, for instance, a number of oscillators, results can be obtained, albeit more laboriously, by the convolution⁶ of the analytical result for the one-dimensional hindered rotor with the sum or density of states of the oscillators.

Appendix

SEPARABLE HARMONIC OSCILLATORS

The quantum partition function for a collection of n independent harmonic oscillators, each of frequency ν_i , is

$$Q_v = \prod_{i=1}^n (1 - \exp(-h\nu_i/kT))^{-1}$$

Let $\omega_i = h\nu_i$ and $\mathcal{E}_i = \exp(-\omega_i \beta)$. Then for separable harmonic oscillators,

$$\begin{aligned} \frac{\partial \ln Q_v}{\partial \beta} &= - \sum_i \frac{\omega_i \mathcal{E}_i}{1 - \mathcal{E}_i} \\ \frac{\partial^2 \ln Q_v}{\partial \beta^2} &= \sum_i \frac{\omega_i^2 \mathcal{E}_i}{(1 - \mathcal{E}_i)^2} \end{aligned}$$

SEPARABLE MORSE OSCILLATORS

The energy ε (in excess of zero-point energy) of a Morse oscillator of frequency ω , quantum number v , and anharmonicity coefficient x (taken to be positive by definition) is

$$\varepsilon = \omega(v - vx - vx^2)$$

The partition function for such oscillator is

$$Q_v = \sum_{v=0}^{v_{\max}} \exp\left(\frac{-\varepsilon}{kT}\right)$$

where

$$v_{\max} = \frac{1}{2} \left(\frac{1}{x} - 1 \right)$$

For a collection of m such oscillators (indexed i), assumed to be independent, the total energy is $E = \sum_i \epsilon_i$ and the total vibrational partition function Q_v is

$$Q_v = \prod_{i=1}^m Q_{vi}$$

$$Q_{vi} = \sum_{v_i=0}^{v_{i,\max}} \exp\left(\frac{-\epsilon_i}{kT}\right)$$

The steepest-descent routine then proceeds normally, except that the various derivatives of Q_{vi} must be obtained by evaluating the sums term by term. The various logarithmic derivatives are then ($\beta = 1/kT$)

$$\frac{\partial \ln Q_{vi}}{\partial \beta} = \frac{\sum_{v_i} \epsilon_i e^{-\epsilon_i \beta}}{Q_{vi}}$$

$$\frac{\partial^2 \ln Q_{vi}}{\partial \beta^2} = \frac{\sum_{v_i} \epsilon_i^2 e^{-\epsilon_i \beta}}{Q_{vi}} - \left(\frac{\sum_{v_i} \epsilon_i e^{-\epsilon_i \beta}}{Q_{vi}} \right)^2$$

If the molecule does not have many low frequencies and the energy and anharmonicity coefficients are not too high, the Morse oscillator representa-

tion is a good approximation to *nonseparable* anharmonic oscillators.¹⁶

References

1. K. S. Pitzer, *J. Chem. Phys.*, **5**, 469 (1937); K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942); J. C. M. Li and K. S. Pitzer, *J. Phys. Chem.*, **60**, 466 (1956).
2. L. Zhu and W. L. Hase, *Chem. Phys. Lett.*, **175**, 117 (1990).
3. T. Beyer and D. F. Swinehart, *Commun. ACM*, **16**, 379 (1973).
4. S. E. Stein and B. S. Rabinovitch, *J. Chem. Phys.*, **58**, 2438 (1973).
5. H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry*, Wiley, New York, 1963, p. 358ff.
6. W. Forst, *Theory of Unimolecular Reactions*, Academic Press, New York, 1973, Chap. 6.
7. M. Abramowitz and A. S. Stegun, *Handbook of Mathematical Functions*, NBS Applied Mathematics Series 55, Washington, 1970, (a) p. 376; (b) p. 591.
8. V. D. Knyazev, I. A. Dubinsky, I. R. Slagle, and D. Gutman, *J. Phys. Chem.*, **98**, 5279 (1994).
9. S. H. Robertson and D. M. Wardlaw, *Chem. Phys. Lett.*, **199**, 391 (1992).
10. D. G. Truhlar, *J. Comput. Chem.*, **12**, 266 (1991).
11. E. B. Wilson, Jr., *Chem. Rev.*, **27**, 17 (1940).
12. J. S. Koehler and D. M. Dennison, *Phys. Rev.*, **57**, 1006 (1940).
13. T. Shimanouchi, *Tables of Molecular Vibrational Frequencies*, NSRDS-NBS 39, Washington, DC, 1972, Vol. I.
14. P. D. Pacey, *Chem. Phys.*, **123**, 329 (1988).
15. W. L. Hase and L. Zhu, *Int. J. Chem. Kinet.*, **26**, 407 (1994).
16. W. Forst, *Chem. Phys. Lett.*, **231**, 43 (1994).